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Gas-phase reaction products and yields of terpinolene with ozone and nitric oxide using a new derivatization agent

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Abstract

The new derivatization agent, *O-tert*-butylhydroxylamine hydrochloride (TBOX) was used to investigate the carbonyl reaction products from terpinolene ozonolysis. With ozone (O_3) as the limiting reagent, four carbonyl compounds were detected: methylglyoxal (MG), 4-methylcyclohex-3-en-1-one, (4MCH), 6-oxo-3-(propan-2-ylidene) heptanal (6OPH), and 3,6-dioxoheptanal (36DOH). The tricarbonyl 36DOH has not been previously observed. Using cyclohexane as a hydroxyl radical (OH•) scavenger, the yields of 6OPH and 36DOH were reduced indicating the influence secondary OH• radicals have on terpinolene ozonolysis products. However, the MG yield increased and the 4MCH yield was unchanged when OH•radicals were scavenged suggesting they are only made by the terpinolene + O_3 reaction. The detection of 36DOH using TBOX highlights the advantages of a smaller molecular weight derivatization agent for the detection of multi-carbonyl compounds. The product yields from terpinolene ozonolysis experiments conducted in the presence of 20 ppb nitric oxide (NO) remained unchanged except for MG which decreased. However, in experiments where O_3 was kept constant at 50 ppb and NO was varied (20, 50, 100 ppb) MG, 6OPH, 36DOH decreased with increasing NO while 4MCH increased with increasing NO. The use of TBOX derivatization if combined with other derivatization agents may address a recurring need to simply and accurately detect multi-functional oxygenated species in air.

Keywords

Ozone; Terpinolene; Carbonyls; Derivatization

1. Introduction

Terpenes are ubiquitous in the indoor environment due to their presence in a variety of cleaning agents and air fresheners (Carslaw, 2013; Singer et al., 2006; Weschler, 2011;

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.10.015.

Weschler et al., 2006). These compounds are highly reactive with indoor oxidants (e.g., OH•, O_3, and NO_3•) due to their unsaturation, and in some cases, steric strain (Kwok and Atkinson, 1995; Nazaroff and Weschler, 2004; Weschler, 2011). This reactivity leads to oxidation of these compounds and formation of products such as aldehydes, ketones, carboxylic acids, organic nitrates and, di-, and tricarbonyls. Highly oxidized species, such as those listed here, have been implicated in a number of deleterious health effects including occupational asthma (Cartier, 2015; Jarvis et al., 2005; Mekenyan et al., 2014; Tarlo and Lemiere, 2014).

Terpinolene (1-methyl-4-(propan-2-ylidene) cyclohexene) is a common terpene used in a variety of floor cleaning products. Recent work by Singer et al. determined the 1 h concentration of terpinolene after the application of a full strength cleaning product to be 900–1300 μg/m^3 (~160–230 ppb) (Singer et al., 2006). Terpinolene's two carbon–carbon double bonds react rapidly with O_3 with measured rate constants ranging from 150 to 190 × 10^{-17} cm^3 $molecule^{-1}s^{-1}$ (Atkinson and Arey, 2003; Stewart et al., 2013). For an indoor O_3 concentration of 50 ppb, this gives a calculated lifetime of 0.12–0.15 h. There have been several investigations of terpinolene ozonolysis chemistry using direct GC-MS analysis and using derivatization agents such as BF_3/methanol and *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) that have led to observation of oxidized species including glyoxal, methylglyoxal, 4-methylcyclohex-3-en-1-one, norpinonaldehyde, and organic acids (e.g. terpinolic acid) (Hakola et al., 1994; Harrison and Wells, 2013; Ma et al., 2008; Yu et al., 1998). The disadvantages of these methods include: thermal instability of the underivatized compounds, observed artifacts in the chromatography from derivatization chemistry, and high molecular weights when derivatizing multiple carbonyls (e.g. PFBHA). Di-, and tricarbonyls can be increasingly difficult to observe when their derivatized molecular weights reach the upper end of the mass range of typical mass spectrometers (i.e. 650 *m/z*).

In this study, terpinolene ozonolysis with and without addition of NO and cyclohexane (OH• scavenger) was investigated using a Teflon® impinger to capture and characterize gas-phase reaction products. Identification of the reaction products (i.e., aldehydes, ketones, and di- and tri-carbonyls) was made using *O-tert*-Butylhydroxylamine hydrochloride, (TBOX) to derivatize the carbonyl products (Wells and Ham, 2014). This method provides the sensitivity, ease of use, and wide-ranging applicability needed for detection of carbonyl compounds at expected indoor air concentrations.

2. Experimental methods

2.1. Chemicals and solvents

All compounds were used as received and had the following purities: from Sigma–Aldrich/Fluka (St. Louis, MO): *O-tert*-Butylhydroxylamine hydrochloride, (TBOX, 99%), terpinolene (90%), toluene (HPLC grade, 99+%), cyclohexane (HPLC grade, 99+%), cyclohexanone (98%), methylglyoxal (40 wt% in water), and glutaraldehyde (50 wt% in water). Water (DI H_2O) was distilled, deionized to a resistivity of 18 MU cm, and filtered using a Milli-Q® filter system (Billerica, MA). Helium (UHP grade), the carrier gas, was supplied by Butler Gas (McKees Rocks, PA) and used as received.

Experiments were carried out at (297 ± 3) K and 1 atmosphere pressure in a 100-L chamber. The chamber/bag was constructed from 5-mil FEP Teflon® film (Welch Fluorocarbon Inc, Dover, NH) and sealed using a W-600T double foot sealer (Sealer Sales, Northridge, CA). Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous calcium sulfate ($CaSO_4$, Drierite, Xenia, OH) and molecular sieves (Drierite) to remove both moisture and organic contaminants. This treated dry air was passed through a mass flow controller into a humidifying chamber and was subsequently mixed with dry air to the pre-determined relative humidity (RH) of 50%. The filler system was equipped with a syringe injection port constructed of a heated 6.4-mm Swagelok (Solon, OH) tee fitting with a 10 mm Ice Blue septum (Restek, Bellefonte, PA). This port facilitated the introduction of liquid reactants into the collapsible chamber. (Wells, 2005). Background measurements of the NIOSH facility air showed concentrations of O_3, NO, and NO_2 at less than 1.0, 1.2, and 0.5 ppb, respectively. All reactant mixtures were generated by this system.

Ozone was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA) in a separate Teflon® chamber. Aliquots of this O_3/air mixture were added to the Teflon® reaction chamber using a gas-tight syringe. Ozone concentrations were measured using a Thermo Electron (Waltham, MA) UV photometric ozone analyzer Model 49C. Aliquots of NO were added to reaction chamber from a 100 ppm tank (Butler Gas, McKees Rocks, PA) using a gas-tight syringe. NO and NO_2 concentrations were measured using a Thermo Electron NO_x analyzer Model 49i.

2.2. Methods

2.2.1. Calibration—Three carbonyl compounds (cyclohexanone, methylglyoxal, and glutaraldehyde), shown in Table 1, were used to calibrate for oxidized products from the terpinolene/O_3 reaction system. Calibration plots were made by analyzing triplicate measurements of standard solutions that were injected into the 100–L Teflon® chamber filled to only 80-L at 50% RH, ranging in concentration from 5 to 30 ppb ($1.2–7.4 \times 10^{11}$ molecules cm^{-3}). Samples were obtained by pulling 60 L of reaction chamber contents using a pump (URG 3000–02Q, Chapel Hill, NC) into 25 mL of deionized water in a 60 mL Teflon® impinger (Savillex, Eden Prairie, MN). After collection, samples were transferred into 40 mL glass vials, then derivatized with 100 µ1 aqueous 250 mM TBOX, and placed in a heated water bath at 70 °C for 2 h. After removing the vial from the water bath and allowing to cool to room temperature, 0.5 mL of toluene was added to the vial. The vial was shaken for 30 s and allowed to separate into a toluene layer and aqueous layer. Then 100 µL of the toluene layer was removed with a pipette and placed in a 2 mL autosampler vial with a 100 µL glass insert (Restek, Bellefonte, PA). One microliter of the extract was injected onto the gas chromatographic/mass spectrometric system (conditions described below).

The extraction efficiency of this method was investigated by collecting five separate 0.5 mL toluene extractions of solutions containing TBOX-derivatized of the standard compounds mentioned above. Each extract was analyzed separately as described above and a comparison of chromatographic peak areas of each derivatized carbonyl indicated that 75%, 20%, and 4% were collected in the first, second and third extractions, respectively. While

combining the three layers would account for 99% of the derivatized carbonyls in the sample, the chromatographic signal would be reduced by about a factor of three due to dilution. In order to maximize the sensitivity of the method, only the first extract was used for chromatographic analysis of both calibration compounds and reaction products (described below). Because both calibration and reaction product samples were treated identically, the observed reaction product yields were not corrected for extraction efficiency.

Experiments were also conducted to determine the collection efficiency of the chamber sampling method described above. A known number of molecules of carbonyls were spiked into 25 mL of DI H_2O in a vial and in a separate experiment injected into the Teflon® chamber and collected as described above. Comparison of the derivatized carbonyls' peak areas between the spiked vials and chamber samples indicated a 50% loss of sample due in part to some sparging in the impinger. Nonetheless, a linear concentration profile was observed for both the spiked and chamber-collected samples.

2.2.2. Terpinolene + O_3 reactions—As with the calibration experiments, the chamber was filled with 80-L of air at 50% RH, then O_3 (20–100 ppb; 0.5–2.5 × 10^{12} molecule cm^{-3}) was added to 1.7 ppm terpinolene (4.25 × 10^{13} molecule cm^{-3}), and allowed to react in the chamber for 30 min. This equilibrium time allowed for efficient mixing and steady-state formation of reaction products. After the reaction, 60 L of sample was collected, at 4 L per minute, into 25 mL of deionized water using an impinger, TBOX derivatized, extracted, and analyzed (as described above). Additional experiments included the addition of 283 ppm (7.0 × 10^{15} molecules cm^{-3}) cyclohexane to the reaction mixture to scavenge OH• formed from Criegee intermediates of terpinolene ozonolysis radicals and/or addition of NO (20–100 ppb, 0.49–2.5 × 10^{12} molecules cm^{-3}) to glean information on NO_X influence on reaction product formation chemistry (Atkinson and Aschmann, 1993; Atkinson et al., 1992; Carslaw, 2013; Criegee, 1975; Forester and Wells, 2011). The results from each of these experiments are described below. Each experiment was done in triplicate.

All samples were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in the electron impact (EI) mode. Compound separation was achieved by an Agilent (Santa Clara, CA) HP-5MS (0.25 mm I.D., 30 m long, 0.25 mm film thickness) column and the following GC oven parameters: 40 °C for 2 min, then 5 °C min^{-1} to 200 °C, then 25 °C min^{-1} to 280 °C and held for 5 min. One μL of each sample was injected in the splitless mode, and the GC injector was returned to split mode 1 min after sample injection, with the following injector temperature parameters: 130 °C for 2 min then 200 °C min^{-1} to 300 °C and held for 10 min. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI ionization spectra were collected from *m/z* 40–650.

3. Results

3.1. Cyclohexanone, methylglyoxal, glutaraldehyde calibration

The three carbonyls (cyclohexanone, methylglyoxal, and glutaraldehyde (Table 1)) were used as surrogates for the calibration of all terpinolene + O_3 reaction products. The following retention times were observed: 12.0 min for singly derivatized cyclohexanone

(MW = 169), 14.5 min for doubly derivatized methylglyoxal (MW= 214), and 20.0, 20.3, 20.5 min for doubly derivatized glutaraldehyde (MW= 242). Calibration plots for the three carbonyls were generated from integrating the peak areas of the total ion chromatograms (TIC) and are shown in the supplementary information, Fig. S1. The limit of detection (determined from three times the integrated baseline peak area) for the four observed compounds (MG, 4MCH, 6OPH, 36DOH) were: 1.4, 2.0,1.2, and 1.2 ppb, respectively.

Derivatization of non-symmetric carbnyls using TBOX typically resulted in multiple chromatographic peaks due to stereoisomers of the oximes. Due to co-elution, not all stereoisomers were chromatographically distinct. Typically an M+1 ion was observed for the derivatized oxime compounds. Retention times for the dicarbonyl oximes were assigned based on derivatization and analysis of solutions containing each dicarbonyl separately. Identification of multiple peaks of the same oxime compound is relatively simple since the mass spectra for each chromatographic peak of a particular oxime are almost identical. In most cases, the *m/z* = 57 ion relative intensity for the chromatographic peaks of the oximes was greater than 50% in the mass spectrum and could be effectively used to generate selected ion chromatograms to identify carbonyl compounds.

3.2. Terpinolene + O_3 experiments

Four main products from terpinolene ozonolysis are listed below and shown in Table 2. Specific product yields for the reactions: terpinolene + O_3, terpinolene + O_3 + CH, and terpinolene + O_3 + NO are shown in Table 3. A two times the standard error of the regression slope was used to determine yield errors reported for in Table 3.

3.2.1. Retention time 14.5 min: methylglyoxal – (MG)—The chromatographic peak for the oxime observed at 14.5 min (labeled peak 1, Fig. 1) has been described previously (Wells and Ham, 2014). Identification and calibration of this oxidation product was confirmed using the standard described above.

3.2.2. Retention time 14.8 min: 4-methylcyclohex-3-en-1-one – (4MCH)—The chromatographic peak for the oxime observed at 14.8 min (labeled peak 2, Fig. 1) was observed as a reaction product of terpinolene + O_3. The main ions (% relative peak height) are 41(40), 57(55), 79(55), 108(55), 125(100), 180(17), 182(20). If 182 *m/z* is the M+1 ion, then a molecular weight of 110 is expected for the carbonyl compound. Based on the ions observed and published reaction mechanisms, the proposed identity of this product in 4-methylcyclohex-3-en-1-one. Further confirmation of this product was made from previous gas-phase terpinolene + O_3 studies using PFBHA as the derivatization agent (Harrison and Wells, 2013). Cyclohexanone's calibration was used to determine the yield of this compound in all experiments.

3.2.3. Retention time 27.4, 27.6, 27.7 min: 6-oxo-3-(propan-2-ylidene) heptanal – (6OPH)—The chromatographic peaks for the oxime observed at 27.4, 27.6, 27.7 min (labeled peak 3, Fig. 1C) were observed as a reaction product of terpinolene + O_3. The main ions (% relative peak height) are 41(35), 57(53), 108(34), 140(31), 164(60), 181(100), 237(42), 254(12), 311(4). If 311 *m/z* is the M+1 ion, then a molecular weight of

168 is expected for a dicarbonyl compound. Based on the ions observed and published reaction mechanisms, the proposed identity of this product in 6-oxo-3-(propan-2-ylidene) heptanal. Further confirmation of this product was made from previous gas-phase terpinolene + O_3 studies using PFBHA as the derivatization agent (Harrison and Wells, 2013). Glutaraldehyde's calibration was used to determine the yield of this compound in all experiments.

3.2.4. Retention time 28.3, 28.5, 28.6, 28.7, 28.9 min: 3,6-dioxoheptanal – (36DOH)—The chromatographic peaks for the oxime observed at 28.3, 28.5, 28.6, 28.9 min (labeled peak 4, Fig. 1C) were observed as a reaction product of terpinolene + O_3. The main ions (% relative peak height), Fig. 2, are 41(28), 57(52), 155(100), 170(18), 187(24), 211(26), 243(13), 282(12), 298(11), 354(7), 356(2). If 356 *m/z* is the M+1 ion, then a molecular weight of 142 is expected for a tricarbonyl compound. Based on the ions observed and proposed reaction mechanism (Fig. S3), the proposed identity of this product in 3,6-dioxoheptanal. This was a newly observed product for the terpinolene + O_3 system. This is the first report of this tricarbonyl as a reaction product of terpinolene ozonolysis. Glutaraldehyde's calibration was used to determine the yield of this compound in all experiments.

4. Discussion

Ozone can react with terpinolene by addition to the endocyclic and/or exocyclic carbon–carbon double bonds (See structure, Table 2). Using AOPWIN v1.92 (EPA, 2000), the calculated ozone addition rate constants to the exocyclic double bond or the endocyclic double bond site are (in units of 10^{-17} cm^3 $molecule^{-1}$ s^{-1}) 120 and 43, respectively. This calculation suggests that O_3 addition to the exocyclic double bond site of terpinolene is favored by almost 3 to 1 over the endocyclic bond site. This is an unusual structural reactivity pattern as other diene terpenes, such as limonene, show the endocylic bond is favored over the exocyclic bond for O_3, OH• and NO_3 addition. Terpinolene may also react with OH• formed as a result of Criegee intermediate decomposition (Atkinson and Aschmann, 1993; Forester and Wells, 2011). As with O_3, OH• can add to either of the carbon–carbon double bond in terpinolene and/or abstract available hydrogens and both reaction pathways lead to oxygenated products. Using AOPWin, the calculated OH• addition reaction rate constants (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) are 110 and 87 for the exocyclic and endocyclic carbon–carbon double bonds, respectively. Unlike O_3 addition, the discrepancy between endocyclic and exocyclic double bonds for OH• addition is much less. Hydroxyl radicals formed during ozonolysis can be efficiently scavenged by using excess concentrations of cyclohexane (Atkinson and Aschmann, 1993; Forester and Wells, 2011). Addition of a scavenger can be used to determine to which oxidation products are formed from ozonolysis alone and/or combination of O_3 and OH•. The influence of OH• on each oxidation product formation is described below.

4.1. Terpinolene + O_3 reaction products

Previous investigations of terpene ozonolysis have resulted in the observation of multiple reaction products (Atkinson, 2003; Atkinson and Arey, 2003; Hakola et al., 1994; Harrison

and Wells, 2013; Ma and Marston, 2009). These observations have been made using various analytical techniques such GC-FTIR, GC-FID, and GC-MS with and without using derivatization agents (e.g. PFBHA, BF_3/methanol). Common oxidation products observed include: mono/di-carboxylic acids and mono/dicarbonyl compounds; however, no tricarbonyl species have been observed previously (Hakola et al., 1994; Harrison and Wells, 2013; Ma and Marston, 2009; Reissell et al., 1999). This may be due to the high molecular weights of the derivatized tricarbonyls (i.e. masses that exceed 750 amu if PFBHA (adds 195 amu per carbonyl) were used for derivatization) or decomposition of the derivatized or underivatized tricarbonyl during GC analyses. Although tricarbonyls have not been observed from terpinolene ozonolysis, the possibility of forming tricarbonyl species has been predicted and detected from other terpene oxidation reactions. The Master Chemical Mechanism v3.3 (University of Leeds, UK) predicts a number of tricarbonyls from the ozonolysis of the terpenes: limonene, α-pinene, and β-pinene. Additionally, Carslaw modeled limonene oxidation by OH• and O_3 and identified the formation of several multi-carbonyl species (Carslaw, 2013). Furthermore, recent gasphase results of limonene ozonolysis with TBOX as the derivatization agent identified the tricarbonyl (3-acetyl-6-oxoheptanal) reaction product which was also predicted by Carslaw's limonene/OH• model (Wells and Ham, 2014). Based on this data, the use of TBOX as a derivatization agent could aid in improving the carbon mass balance from terpene ozonolysis reactions.

Methylglyoxal (MG) is an oxidation product observed from terpinolene ozonolysis that is most likely generated through primary and secondary reaction processes. It is possible that MG is a primary product formed during O_3 addition to the exocyclic carbon–carbon double bond to form 4MCH. However, in this proposed scenario one would expect the yield of MG (0.10 ± 0.01) and 4MCH (0.32 ± 0.04) to be similar (Table 3). This suggests that MG further decomposes on separation from the ring or it is formed as the ring itself decomposes from ozone addition to the endocyclic carbon–carbon double bond. Interestingly, when OH• is scavenged in the terpinolene + O_3 system the yield of MG (0.14 ± 0.02, Table 3) is larger than the yield from terpinolene + O_3 suggesting that OH radicals may remove MG ($k_{OH + MG} = 15 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) (Atkinson, 2003) or OH radicals react with a MG precursor. The addition of 20 ppb (4.92×10^{11} molecules cm^{-3}) NO to the reaction system had no significant effect on the overall yield of MG (Table 3).

Ozone addition to the exocyclic double bond leads to the formation of 4MCH as previously described (Harrison and Wells). The 0.33 ± 0.04 yield of 4MCH (Table 3) from the terpinolene + O_3 (OH• scavenged) reaction, reported here, coincides with the previously measured yields: 0.28 ± 0.06 (Harrison and Wells, 2013), 0.40 ± 0.06 (Hakola et al., 1994), 0.40 ± 0.08 (Reissell et al., 1999), and 0.50 ± 0.05 (Ma and Marston, 2009). The high yield reported here and previously for this reaction was expected as O_3 addition to exocyclic double bonds and subsequent reactions are favored. The similar yields of 4MCH for the terpinolene + O_3 (0.32 ± 0.04) and terpinolene + O_3 (OH• scavenged, 0.33 ± 0.04) reactions indicate that OH• does not contribute to its formation and thus 4MCH is a primary reaction product. This was unexpected as the terpinolene + OH• rate under the experimental conditions is quite fast (2.25×10^{-10} cm^3 $molecule^{-1}$ s^{-1}) (Aschmann et al., 2002) which would likely result in the formation of 4MCH or 6OPH. This suggests that in this experimental system OH• may preferentially react with something else, such as terpinolene,

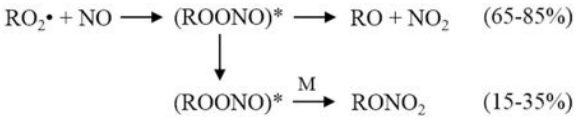
over 4MCH (AOP-Win calculated $k_{OH + 4MCH} = 9 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) or terpinolene. The addition of 20 ppb (4.92×10^{11} molecules cm^{-3}) NO to the reaction system had no significant effect on the overall yield of 4MCH (Table 3).

The dicarbonyl (6OPH) can be formed through O_3 or OH• (generated from Criegee intermediate decomposition) addition to the endocyclic double bond as previously described (Harrison and Wells, 2013). Based on the observed results, OH• addition is the primary route to 6OPH formation as a 67% reduction in yield was observed in comparing the terpinolene + O_3 and terpinolene + O_3 (OH• scavenged) experimental systems; 0.05 ± 0.01 vs 0.017 ± 0.004, respectively. Hakola et al. reported the yield of 6OPH (≤0.02) for the terpinolene + O_3 (OH• scavenged) reaction which is comparable to the yield reported (under OH• scavenged conditions) here, 0.017 ± 0.004 (Hakola et al., 1994). Additionally, comparing the observed yield of 4MCH (0.33 ± 0.04) to 6OPH (0.017 ± 0.004) further supports the notion that for terpinolene exocyclic O_3 addition is a more favored reaction pathway. The addition of 20 ppb (4.92×10^{11} molecules cm^{-3}) NO to the reaction system had no significant effect on the overall yield of 6OPH (Table 3).

There are three potential mechanisms for the formation of the newly observed tricarbonyl (36DOH). In the terpinolene + O_3 experiments, OH• radicals generated via Criegee decomposition can add to the endocyclic carbon–carbon double bond of 4MCH (Fig. S3). Subsequent reactions with O_2 and alkoxy radicals lead to formation of the stabilized tricarbonyl. This seems like a reasonable pathway since the 36DOH yield was reduced by 73% when OH• was scavenged. Secondly, it is possible that 36DOH may have been formed through secondary O_3 and/or OH• addition to the carbon–carbon double bond of 6OPH. This pathway seems unlikely for two reasons: 1) this potential reaction mechanism would suggest a yield of 36DOH (0.021 ± 0.003) (Table 3) that would be dependent on 6OPH (0.017 ± 0.004) yield, yet it can be seen that 36DOH and 6OPH yield measurements are of similar magnitude suggesting two independent formation routes and 2) since 6OPH concentrations are small (>7.4×10^{10} molecule cm^{-3} (3 ppb)) in this experimental system it is unlikely that the OH• addition rate to 6OPH would effectively compete with other possible OH• addition/H-abstraction pathways. Lastly, 36DOH could be made via O_3 addition to the exocyclic double bond of terpinolene and as the Criegee intermediate begins to break apart, an adjacent H from either of the terminal methyl groups may be extracted. The newly formed OH• moiety can possibly add to the endocyclic carbon–carbon double bond (Kumar et al., 2014a) instead of entering the gas phase. Subsequent breaking of the endocyclic double bond leads to a biradical which further reacts with O_2 to form 36DOH (Fig. S3). This pathway is supported by the observation that the 36DOH yield is not zero (0.021 ± 0.003) even when OH• is scavenged. There has been recent work on the modeling of Criegee intermediates or carboxylic acid catalyzed Criegee intermediate reaction that could support this alternate mechanism (Kumar et al., 2014a, b, c). The addition of 20 ppb (4.92×10^{11} molecules cm^{-3}) NO to the reaction system had no significant effect on the overall yield of 36DOH (Table 3).

4.2. NO effect on terpinolene ozonolysis

Recent modeling of VOC oxidation by O_3, OH•, and NO_3• in the presence of NO_x highlighted the significance of NO on the VOC oxidation rate (Waring and Wells, 2015). In the model, the addition of NO resulted a reduced impact of ozonolysis on VOC oxidation due to scavenging of O_3 by NO. Additionally, NO reacts with alkyl peroxy radicals (RO_2•) to form RO•, which can stabilize to form carbonyls, or through addition and isomerization form alkyl nitrates (Finlayson-Pitts and Pitts, 2000).



In a low NO/high VOC environment such as the terpinolene system described here, the current data suggests that the formation of $RONO_2$ is more likely because this species is the primary terminator in the NO to NO_2 cycle for larger organic compounds (Perring et al., 2013). Evidence suggesting organic nitrate formation can be seen in Fig. 3 as MG, 6OPH and 36DOH concentrations decrease as NO concentration increases at a fixed O_3 concentration. Initially, 4MCH concentration decreases upon initial NO addition to the reaction systems, but increases as NO concentration increases. This could be due to the formation of additional OH• by:

$$HO_2 + NO \rightarrow OH\cdot + NO_2 \quad K_{HO_2 + NO} = 9.6 \times 10^{-12} cm^3 s^{-1} \text{ (Bohn and Zetzsch 1997)}$$

where OH• can add to the exocyclic double bond of terpinolene to form 4MCH. It is unlikely that O_3 could react with NO to eventually form NO_3 as O_3 is more likely to react with terpinolene (1.7 ppm, reaction rate = 0.08 s^{-1}) than NO (100 ppb, reaction rate = 0.045 s^{-1}). While some O_3 is likely lost due to reaction with NO, the predominate O_3 loss is through reaction with terpinolene. It is interesting to note that MG concentration, which could be formed from the exocyclic OH• addition decomposition, decreases as NO concentration increases. This may suggest that the observed reduction in MG concentration is the result of the formation of a multifunctional $RONO_2$ such as a hydroxy nitrate which would not be detected by TBOX derivatization. When OH• is scavenged, the MG concentration doubles even in the presence of 20 ppb NO, which may also suggest the formation of a hydroxy nitrate since both OH• and NO might be needed to form this species. The increase in 4MCH in the OH• scavenged terpinolene/O_3/NO system is not as easily explained. The gas-phase concentration of 4MCH may be affected by the presence of secondary organic aerosols (SOA). There may be a slight fraction of 4MCH partitioning into SOA. It has been suggested that SOA concentrations may be reduced in the presence of NO_x, in this case NO, which could result in an increase in 4MCH concentration (Donahue et al., 2005). The removal of two loss pathways for 4MCH (partitioning into particulate matter and reaction with OH• radicals) would be possible in the terpinolene/O_3/NO/cyclohexane system.

While the derivatization method described here has several advantages, there can be some limitations. These include: multiple molecular structures for carbonyls with the same molecular weight, no detection of other oxidation products such as carboxylic acids, alcohols and organic nitrates, and possible difficulty extracting multi-functional oxidation products such as organic nitrate/carbonyls and/or carboxylic acid/carbonyls. The use of water as the impinger solvent, though convenient, may also prevent capture of more hydrophobic oxidation products during collection (e.g. organic nitrate moiety) and/or prevent extraction of hydrophilic compounds due to enhanced solubility (e.g. carboxylic acid moiety).

5. Conclusion

The ozonolysis of terpinolene in the gas phase was investigated using a new carbonyl derivatization agent, O-*tert*-butylhydroxylamine hydrochloride (TBOX). The carbonyl product yield per unit ozone molecule reacted with terpinolene was determined with and without scavenging secondary OH• radicals for: methylglyoxal (MG), 4-methylcyclohex-3-en-1-one, (4MCH), 6-oxo-3-(propan-2-ylidene) heptanal (6OPH), and 3,6-dioxoheptanal (36DOH). Due in part to the lower molecular weight of TBOX, the tricarbonyl species, 36DOH, was detected for the first time. The scavenging of secondary OH• reduced the yields of MG, 6OPH, and 36DOH highlighting the significance of OH•'s role in the overall terpinolene oxidation. The ozonolysis of terpinolene was also investigated in the presence of NO and the formation of MG was the most affected suggesting a possible route in forming organic nitrates. Future investigations of single and mixtures of terpenes using other derivatization agents with TBOX are planned. Clearly the introduction of NO to the reaction system has an effect on the reaction mechanism and further supports the need to characterize the $RONO_2$ species in the indoor environment.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

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HIGHLIGHTS

- Aqueous collection and derivatization of gas-phase terpinolene ozonolysis products.
- Multi-functional gas-phase carbonyls detected from terpinolene ozonolysis.
- Hydroxyl radical's and nitric oxide's influence on reaction product formation.

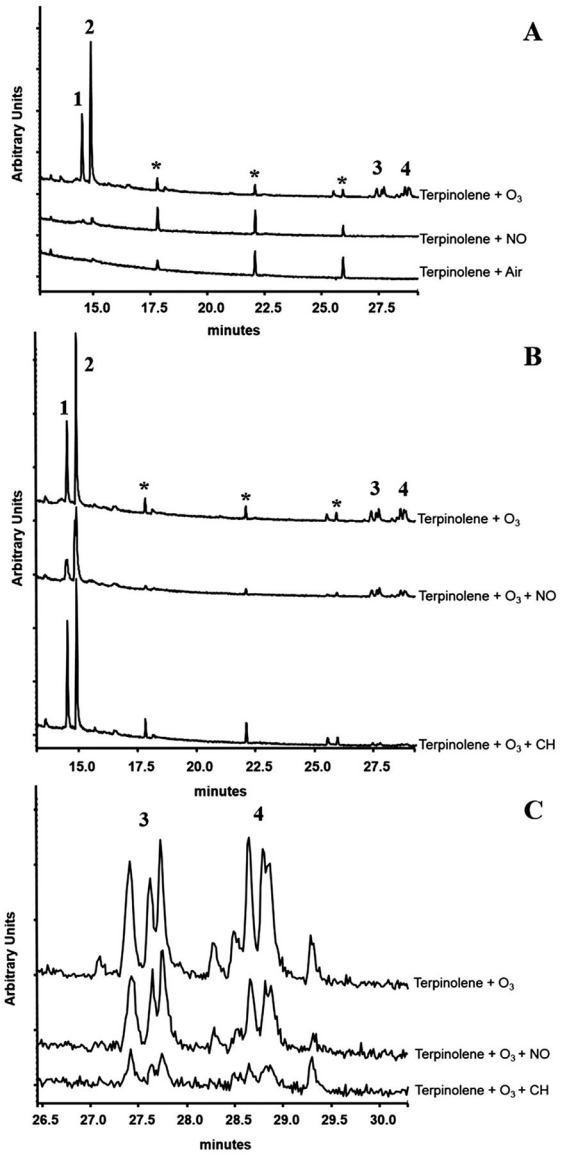


Fig. 1.

Chromatograms of the terpinolene gas-phase system. "*" indicate contaminant peaks from septa, 1 = MG, 2 = 4MCH, 3 = 6OPH, 4 = 36DOH. A) Stacked chromatograms comparing terpinolene + O_3, terpinolene with NO, and terpinolene in air. B) Stacked chromatograms comparing terpinolene + O_3, terpinolene + O_3 + NO, terpinolene + O_3+ cyclohexane (OH radical scavenger). C) Expanded chromatogram for dicarbonyl and tricarbonyl species under same conditions as noted in B).

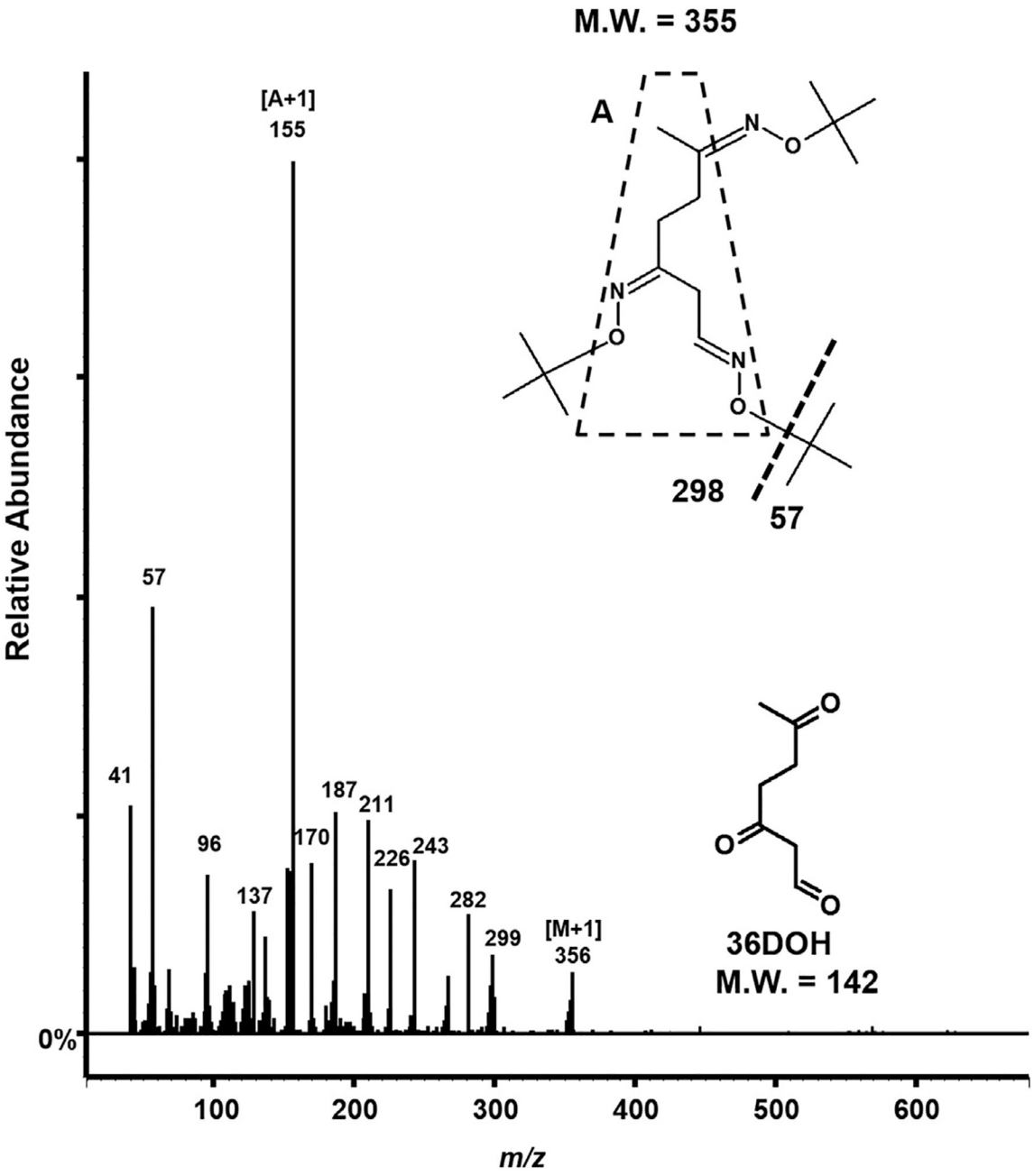


Fig. 2.

Mass spectrum of the derivatized tricarbonyl species. The un-derivatized structure is shown in lower right corner.

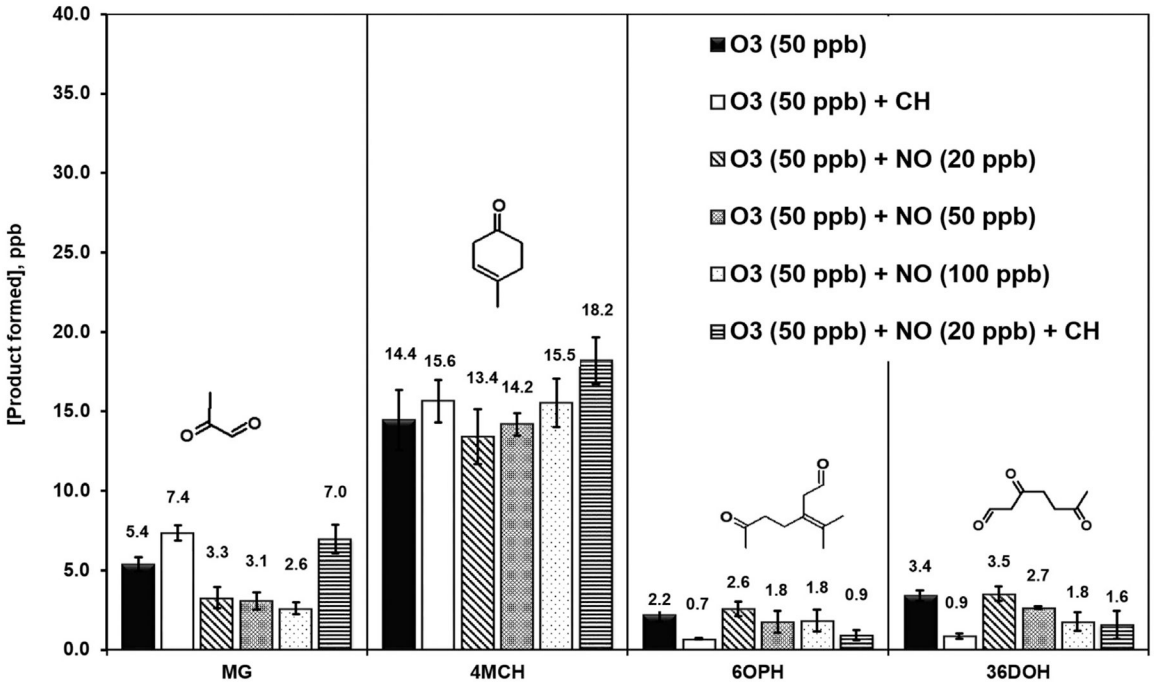


Fig. 3.

Product concentration as a function of added NO and cyclohexane (CH) to scavenge OH radicals. The standard deviation of the data values is represented by the error bars.

Table 1

Compounds used for system calibration. Chromatographic retention time, structure and molecular weight and observed ions are listed.

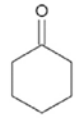
Ret. time (min.)	Structure (name)	Derivatized M.W.	EI ions (rel. intensity)
12.0	M.W. = 98		
		169	41(60),57(90), 67(30), 81(35), 96(40), 114(100), 170(40)
	(cyclohexanone)		
14.5	M.W. = 72		
		214	41(25), 57(100), 102(100), 158(25), 215(20)
	(methylglyoxal)		
20.0 20.3 20.5	M.W. = 100		
		242	41(40), 57(100), 113(100), 130(100), 186(40), 242(2), 243(2)
	(glutaraldehyde)		

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Table 2

Reaction products observed from terpinolene ozonolysis. Chromatographic retention time, structure and molecular weight and observed ions are listed.

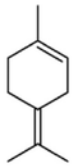
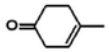
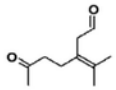
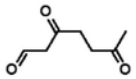
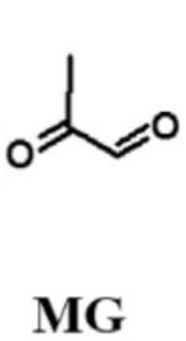
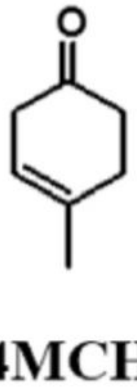
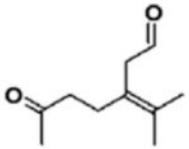
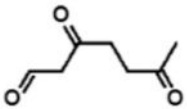
Ret. time (min.)	Structure (name)	Derivatized M.W.	EI ions (rel. intensity)
	 Terpinolene M.W. = 136		
14.5	M.W. = 72  methylglyoxal (MG)	214	41(25), 57(100), 102(100), 158(25), 215(20)
14.8	M.W. = 110  4-methylcyclohex-3-en-1-one (4MCH)	181	41(40), 57(55), 79(55), 108(55), 125(100), 180 (17), 182(20)
27.4 27.6 27.7	M.W. = 168  6-oxo-3-(propan-2-ylidene)heptanal (6OPH)	310	41(35), 57(53), 108(34), 140(31), 164(60), 181(100), 237(42), 254(12), 311(4)
28.3 28.5 28.6 28.7 28.9	M.W. = 142  3,6-dioxoheptanal (36DOH)	355	41(28), 57(52), 155(100), 170(18), 187(24), 211(26), 243(13), 282(12), 298(11), 354(7), 356(2)

Table 3

Molar yields of reaction products under different experimental conditions. CH = cyclohexane (OH radical scavenger). Errors are two times standard error of regression.

Experiment	Molar yields			
	 MG	 4MCH	 6OPH	 36DOH
Terpinolene + O_3	0.10 ± 0.01	0.32 ± 0.04	0.05 ± 0.01	0.08 ± 0.01
Terpinolene + O_3 + CH	0.14 ± 0.02	0.33 ± 0.04	0.017 ± 0.004	0.021 ± 0.003
Terpinolene + O_3 (20 ppb NO)	0.09 ± 0.01	0.33 ± 0.05	0.053 ± 0.004	0.08 ± 0.01